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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C09B 69/10, C08J 3/09		A1	(11) International Publication Number: WO 92/07913
(21) International Application Number: PCT/US91/07854		(74) Agent: GRAVES, Bernard, J., Jr.; 343 State Street, Rochester, NY 14650-2201 (US).	
(22) International Filing Date: 28 October 1991 (28.10.91)			
(30) Priority data: 604,311 29 October 1990 (29.10.90) US		(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).	
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(54) Title: POWDER COLORANT COMPOSITIONS AND PROCESS FOR THE PREPARATION THEREOF

(57) Abstract

Disclosed are powder colorant compositions in a finely-divided form and process for the preparation therefor.

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POWDER COLORANT COMPOSITIONS AND
PROCESS FOR THE PREPARATION THEREOF

Field of the Invention

5 This invention belongs to the field of polymer chemistry. More particularly, this invention relates to polyester powder colorant compositions and a process for their preparation.

10 Background of the Invention

Plastics, paints, printing inks, rubber, cosmetics and similar materials typically are colored by organic pigments when superior brilliance and tinctorial strength are important. Toxicity considerations have been a chronic problem relative to the use of organic dyes and pigments since some have been shown to be potential carcinogens and to cause contact dermatitis. Plastics usually contain various additives such as fillers, plasticizers, colorants, etc. The polymeric base of such plastics normally does not produce allergic or other adverse reactions by themselves but leachable or extractable additives are known [Fregert, Manual of Contact Dermatitis, Munksgard Denmark (2nd Ed. 1981)] to cause contact dermatitis.

25 Various processes for the manufacture of finely-divided forms of polyesters have been disclosed in the prior art such as U.S. Patents 4,378,228, 4,254,207, 3,586,654, 3,931,082, 4,267,310, 4,305,864, 4,451,606, 3,674,736 and 3,669,922. Some of these known processes include the presence of pigments such as carbon black during particle size reduction to produce colored polyester powders. The known procedures are summarized below.

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1. Comminution, as by grinding, which is difficult and expensive and results in highly irregular-shaped particles having a broad range of particle size distribution.
- 5 2. Spray drying techniques which tend to produce "hollow shells" or porous particles and also are hazardous when organic solvents are used to dissolve the polyester.
- 10 3. Dispersion processes which involve melting the polymer in an inert solvent in the presence of a non-ionic dispersing agent. Polyester, in contrast to other thermoplastic polymers, tends to hydrolyze (decompose) when melted in the presence of water and the particles thus produced have a strong tendency to agglomerate or coalesce.
- 15 4. Heating under shearing agitation conditions a condensation polymer in an aprotic liquid which is not a solvent for the polymer and in the presence of a dispersing agent to form small liquid particles upon cooling with agitation. Colorants added during this process are still extractable, sublimable, and may exude from the polymer.
- 20 5. Solvent induced crystallization wherein an amorphous polymer is initially contacted with a crystal-inducing fluid under certain conditions while the polymer is subjected to physical and/or ultrasonic forces. Colorants added during this process are not reacted with the polymer and therefore are subject to removal from the polymer.
- 25 6. Producing microcrystalline polyesters by a hydrolytic removal of amorphous regions of synthetic, linear polyesters followed by a

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mechanical disintegration of the resulting aggregated microcrystals.

7. Crystallization of polyesters in the presence of nucleating agents.

5 However, the prior art does not disclose the preparation of colored microcrystalline polyester powders wherein an amorphous or partially-crystalline polyester, having a thermally-stable, colorant compound copolymerized therein, is converted to a colored, microcrystalline, 10 polyester powder by means of a dissolution-crystallization-precipitation procedure. The prior art also fails to disclose microcrystalline, polyester powders containing high levels of colorant incorporated therein which cannot be removed by extraction or 15 sublimation and which does not exude from the surface of the polymer.

It is known that thermoplastic polymeric materials may be colored using color concentrates consisting of physical admixtures of polymers and colorants. However, 20 the use of such physical admixtures to color polymeric materials such as polyesters, e.g., poly(ethylene terephthalate) and blends thereof, presents a number of problems:

(1) Colorant migration during drying of the 25 colored polymer pellets.

(2) Colorant migration during extrusion and colorant accumulation on dies which can cause film rupture and shut-downs for clean-up, etc. Such colorant migration and accumulation result in time consuming and difficult clean-up when a polymer of another color is 30 subsequently processed in the same equipment.

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(3) Colorants may not mix well, for example, when using two or more color concentrates to obtain a particular shade.

(4) Colorants may diffuse or exude during storage of the colored polymeric material.

5 Further, the presence of oligomeric material in the polymers, such as polyester, admixed with the colorants to produce the known color concentrates can cause problems of equipment contamination during processing.

10

Summary of the Invention

This invention pertains to novel, powder colorant compositions comprising a semicrystalline polyester, in a finely-divided form, having copolymerized therein one 15 or more colorant compounds at levels greater than about 1 weight percent. This invention also pertains to a process for the preparation of such colorant compositions comprising dissolution of an amorphous or partially-crystalline polyester color concentrate in a 20 crystallization-inducing solvent or mixture of solvents followed by crystallization or crystallization-precipitation. The colorant compositions have utility in a variety of end uses where nonextractability of the colorant is important.

25

Detailed Description of the Invention

The powder colorant compositions provided by this invention comprise a semicrystalline polyester, in a finely-divided form, having copolymerized therein at 30 least 1, more typically at least 5, weight percent, based on the total weight of the compositions, of the residue of a thermally-stable, difunctional colorant compound. Since the powder compositions have colorant

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residues incorporated into the polymer chain; the colorant is not leachable, sublimable or extractable and does not exude from the composition. The colorant compositions are in the form of a finely-divided, 5 colored microcrystalline polyester powder capable of being used in a wide variety of products such as cosmetics, skin creams or lotions, soaps, hair colorations, waxes, polishes, coatings, paints, toners for impactless printing, inks, etc., which will be safe 10 to humans since exposure to toxic molecules readily absorbed by the body is greatly minimized. Thus, the colorant compositions have utility in a wide variety of applications where toxicological concerns are evident. The concentrate materials may be used for imparting 15 color to a wide variety of thermoplastic compositions including polyesters, polycarbonates, polyamides, cellulose esters, polyurethanes, polyolefins, etc., by conventional melt or solution blending techniques. When using the polymeric color concentrates of this invention, the colorant problems relative to toxicity 20 concerns are largely overcome.

The powder colorant compositions provided by this invention may be obtained by means of a dissolution-crystallization-precipitation procedure wherein a 25 polyester color concentrate, preferably an amorphous or partially crystalline polyester color concentrate, is dissolved in an organic solvent from which the colorant composition is recovered in a finely divided form consisting of particles of relatively uniform size, e.g., from about 10 to 50 microns.

The color concentrates which may be used in the preparation of the powder colorant compositions of the present invention comprise crystalline, semi-crystalline

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and amorphous polyesters having copolymerized therein at least 1.0, preferably at least 5.0, weight percent of the residues of at least one thermally-stable, difunctional colorant compound. The concentration of 5 the colorant residue in the polyester is dependent on such factors as the end use for which a particular concentrate is designed, the polyester being used, and the physical characteristics required of the color 10 concentrate. Normally, the color concentrates will not contain more than about 50 weight percent of colorant residues with a concentration in the range of about 10 to 40 weight percent being more common. Typically, the polyester color concentrates have an inherent viscosity 15 of at least 0.20 and are comprised of (i) a diacid component consisting of the residues of one or more dicarboxylic acids, (ii) a diol component consisting of the residues of one or more diols and (iii) a colorant component consisting of the residues of one or more thermally-stable, difunctional colorant compounds. The 20 concentration of colorant component (iii) and inherent viscosity are interrelated to the extent that the degree of polymerization and the inherent viscosity should be sufficiently high to ensure that substantially all of the colorant compound is reacted into the polymer and, 25 preferably, into polymer chains which are not extractable. Thus, for example, when the concentration of colorant component (iii) is 20 weight percent or higher, the inherent viscosity of the polyester normally will be about 0.25 or higher.

30 The diacid residues may be derived from aliphatic, alicyclic, or aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,4-cyclohexane-dicarboxylic acid, 1,3-cyclohexanedicarboxylic acid,

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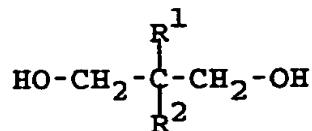
succinic acid, glutaric acid, adipic acid, sebacic acid, 1,12-dodecanedioic acid, 2,6-naphthalenedicarboxylic acid and the like. In the polymer preparation, it is often preferable to derive the diacid residues from an ester-forming derivative of the dicarboxylic acid such as the dimethyl, diethyl, or dipropyl esters. The anhydrides or acid halides of these acids also may be employed where practical.

The diol components of the described polyesters may be selected from ethylene glycol, 1,2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-butane-dioli, 2,2-dimethyl-1,3-propanediol, 1,6-hexanediol, 1,10-decanediol, 1,12-dodecanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, X,8-bis-(hydroxymethyl)-tricyclo-[5.2.1.0]-decane wherein X represents 3, 4, or 5; and diols containing one or more oxygen atoms in the chain, e.g., diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, 1,3- and 1,4-bis(2-hydroxyethyl)benzene and the like. In general, these diols contain 2 to 18, preferably 2 to 12 carbon atoms. Cycloaliphatic diols can be employed in their cis or trans configuration or as mixtures of both forms.

The preferred amorphous color concentrates from which our novel powder colorant compositions may be prepared exhibit a glass transition temperature (Tg) and no, or only a trace of, crystallization or melting point by differential scanning calorimetry (DSC). Examples of such amorphous polyesters include those obtained by the polymerization of a difunctional colorant compound,

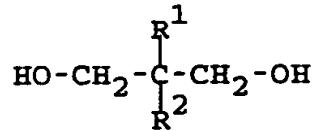
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terephthalic and/or 2,6-naphthalenedicarboxylic acid and a branched-chain diol having the formula



wherein R¹ is hydrogen or an unsubstituted or substituted alkyl, cycloalkyl or aryl radical, and R² is an unsubstituted or substituted alkyl, cycloalkyl or aryl radical. Preferred amorphous polyester color concentrates have an inherent viscosity of about 0.2 to 0.8 and are comprised of:

- (i) diacid residues comprised of at least 50, preferably at least 80, mole percent terephthalic and/or 2,6-naphthalenedicarboxylic acid residues;
- (ii) diol residues comprised of at least 50, preferably at least 80, mole percent of residues of a diol having the formula



wherein R¹ is hydrogen or lower alkyl and R² is lower alkyl; and

- (iii) residues of a thermally-stable, difunctional colorant compound.
- The particularly preferred amorphous polyester color concentrates are comprised of (i) diacid residues consisting essentially of terephthalic and/or 2,6-naphthalenedicarboxylic acid residues; (ii) diol residues consisting essentially of 2,2-dimethyl-1,3-propanediol residues; and (iii) residues of one or more colorant compounds.

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Other amorphous polyesters, as defined above, suitable for preparing the powder colorant compositions may be obtained by employing (1) two dicarboxylic acids and one or more diols or (2) two diols and one or more dicarboxylic acids according to known procedures for obtaining amorphous polyesters. The polyester comprising a diacid component consisting of 75 mole percent terephthalic acid residues and 25 mole percent 1,4-cyclohexanedicarboxylic acid residues, a diol component comprised of 1,4-butanediol residues and residues of a difunctional colorant compound of Formula (I) is an example of such a polyester.

The partially-crystalline color concentrates useful in the preparation of the powder colorant compositions of this invention usually exhibit a glass transition temperature, a crystallization temperature and a melting temperature by DSC. These partially-crystalline, polyester concentrates are comprised of (i) diacid residues consisting of at least 80 mole percent terephthalic acid residues, 2,6-naphthalenedicarboxylic acid residues, 1,3-cyclohexanedicarboxylic acid residues, 1,4-cyclohexanedicarboxylic acid residues or a mixture thereof, (ii) diol residues comprised of at least 50 mole percent of residues having the formula $-O-(CH_2)_p-O-$ wherein p is 2, preferably 4, to 12 and (iii) residues of a thermally-stable, difunctional, colorant compound. A preferred partially-crystalline color concentrate has a melting temperature of at least 110°C and is comprised of (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues, (ii) diol residues comprised of at least 80 mole percent of residues of 1,4-butanediol and (iii) residues of the colorant compound. An especially preferred partially-crystalline

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color concentrate has a melting temperature of at least 110°C and consists essentially of (i) terephthalic acid residues, (ii) 1,4-butanediol residues and (iii) residues of one of the difunctional, colorant compounds described hereinbelow.

The polyester color concentrates may be prepared according to conventional esterification or transesterification and melt polycondensation procedures using (i) a dicarboxylic acid or, preferably, a lower alkyl ester thereof, (ii) a diol and (iii) a thermally stable colorant compound bearing two reactive groups.

Normally, a 50 mol percent excess of the diol is used. The colorant compound preferably is added with the other monomers at the commencement of the color concentrate manufacture although it may be added subsequently, e.g., at the beginning or during the polycondensation step. The concentration (weight percent) of the colorant residue is determined by summing up the weights of all the components charged to the reactor and subtracting the sum of the weights of the components removed during transesterification and polycondensation, e.g., methanol and excess diol. The difference represents the theoretical yield of the color concentrate. The weight of the colorant charged to the reactor is divided by the theoretical weight and multiplied by 100 to give the weight percent of colorant residue.

The thermally-stable, difunctional, colorant compounds useful in the preparation of the polyester color concentrates and, thus, the powder colorant compositions of the present invention may be selected from a wide variety of colorant compounds of diverse structure types and/or classes. The only requirements

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of useful colorant compounds is that (1) they are stable under polyester polymerization conditions and (2) their structures bear at least two polyester-reactive substituents. Examples of the types or classes of colorant compounds which may be used include methines, bis-methines, anthraquinones, 2,5-diarylaminoterephthalic acids, quinophthalones, thioxanthones, 3H-dibenz[f,ij] isoquinoline-2,7-diones (anthrapyridones), 7H-dibenz[f,ij]isoquinoline-7-ones (anthrapyridines), 10 7H-benz[e]perimidine-7-ones, 7-amino-2H-1-benzopyran-2-ones (coumarins), triphenodioxazines, 5,12-dihydro-quinoxalino [2,3-b]phenazines (fluorindines), phthaloylpyrrocolines, 4-aminonaphthalimides, 3,6-diaminopyromellitic acid dimides, benzanthrones, 15 naphtho[1',2',3':4,5]quino[2,1-b]quinazoline-5,10-diones, 6,15-dihydro-5,9,14,18-anthrazinetetrones (indanthrones), 5H-benzo[a]phenoxazine-5-ones, 6H,13H-pyrido[1,2-a:3,4-b] diindole-6,13-diones, diindolo-[3,2,1-de-3',2',1'-ij][1,5] naphthyridine-6,13-diones, 20 perylenes, perinones, naphthalene-1,4,5,8-tetracarboxylic acids and diimides, quinacridones and phthalocyanines. Specific examples of suitable colorant compounds are described in U.S. Patents 3,417,048, 3,489,713, 4,080,355, 4,088,650, 4,049,376, 4,116,923, 4,267,306, 25 4,359,570, 4,403,092, 4,594,400, 4,740,581, 4,745,173, 4,617,373, 4,804,719, 4,808,677 and 4,892,922, incorporated herein by reference, and British Patent 1,225,566.

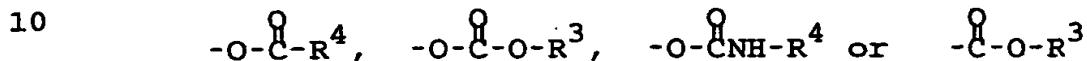
The colorant compounds described above may be 30 represented by the formula



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wherein Col is the residue of one of the types of colorants set forth above and X is a polyester-reactive substituent, i.e., a group reactive with at least one of the monomers from which the polyester is prepared.

5 Examples of the reactive groups which X may represent include hydroxy, carboxy, an ester radical, amino, alkylamino, and the like. The ester radicals may be any radical having the formula



15 wherein R^3 is selected from unsubstituted or substituted alkyl, cycloalkyl or aryl radicals. R^3 preferably is unsubstituted alkyl, e.g., alkyl of up to about 8 carbon atoms, or phenyl, and most preferably, lower alkyl, e.g., methyl and ethyl. R^4 is hydrogen or selected from those groups listed for R^3 . Reactive group X preferably is hydroxy, carboxy, carbalkoxy, or alkanoyloxy of up to about 4 carbon atoms, e.g., carbomethoxy or acetoxy. Known colorant compounds may, if necessary, be functionalized by the addition thereto 20 of reactive groups represented by X according to known procedures.

25

The powder colorant compositions described hereinabove may be prepared in accordance with the present invention by a dissolution-crystallization-precipitation process comprising the steps of:

30 (1) dissolving in an inert, organic solvent a polyester color concentrate comprising a crystalline or, preferably, a partially crystalline or amorphous polyesters having copolymerized therein at least 1.0, preferably at least 5.0, weight percent of the residues of at least one thermally-stable,

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difunctional colorant compound, e.g., a compound of formula (I); and

(2) precipitating from the solution of step (1) the semicrystalline colorant composition in a finely divided form consisting of particles of relatively uniform size, e.g., from about 10 to 50 microns.

If desired, the particle size of the powder colorant compositions obtained from the process may be reduced further by conventional grinding processes.

Typically, step (1) is carried out using a solvent in which the polyester color concentrate is soluble to the extent of at least 100 g concentrate per liter of inert solvent. Examples of solvents in which the amorphous and/or partially-crystalline concentrates may be dissolved include halogenated hydrocarbons such as aliphatic chlorides, e.g., methylene chloride; alkyl carboxylic acid esters containing 3 to about 10 carbon atoms, e.g., ethyl acetate and methyl benzoate; hydrocarbons such as toluene; and ethers such as tetrahydrofuran. We have found methylene chloride to be a particularly effective solvent.

The amount of solvent required may vary substantially depending on the particular inert solvent or combination of inert solvents used, the particular polyester color concentrate used and the temperature at which the dissolution is carried out. Typically, the ratio of the concentrate:solvent (weight:weight) is in the range of about 1:3 to 1:15, preferably about 1:4 to 1:8. The temperature at which the dissolution step is performed may be in the range of about 25°C up to the boiling point of the solvent.

The second step of the process may be accomplished by cooling the step (1) solution, with or without a

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reduction in the volume of solvent, i.e., either with or without a solution concentration step. Another useful technique involves adding to the step (1) solution a miscible, inert, organic liquid/solvent (usually having 5 a higher boiling point) which causes crystallization and precipitation of the colored semicrystalline powder, either with or without partial, or essentially complete, removal of the step (1) solvent by distillation. The use of methylene chloride as the step (1) solvent and an 10 alkyl acetate such as ethyl acetate as the "crystallization-inducing" solvent has been found to be particularly efficacious and preferred.

Depending on their intended utility, the powder colorant compositions obtained in accordance with our 15 novel process may be extracted with a suitable organic solvent to remove relatively low molecular weight polyester oligomers. Examples of oligomer-extracting solvents include ketones such as acetone, 2-pentanone, 3-methyl-2-butanone, 4-methyl-2-pentanone, 2-hexanone 20 and 5-methyl-2-hexanone; hydrocarbons such as hexane, heptane and toluene; and ethers such as tetrahydrofuran. Another, but not preferred, dissolution-precipitation procedure involves dissolving an amorphous color 25 concentrate in certain solvents, e.g., ethyl acetate, from which the polymeric color concentrate, after undergoing a change in morphology, precipitates.

Some of the more crystalline polyesters such as poly(ethylene terephthalate) and poly(tetramethylene terephthalate) require the use of a high-boiling solvent 30 in the dissolution-precipitation procedure. Examples of such high-boiling solvents include alkyl esters of aromatic mono- and di-carboxylic acids, e.g. alkyl benzoates and alkyl phthalates; aliphatic dicarboxylic

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acid esters; glycol esters, e.g., ethylene glycol diacetate; diethylene glycol diacetate; aromatic ketones, e.g., acetophenone; aromatic oxides, e.g. diphenyl oxide; aliphatic carboxamides, e.g.

5 N,N-dimethylformamide; isophorone. Methyl benzoate and ethylene glycol diacetate are particularly preferred high-boiling solvents since they are readily available, have a pleasant odor and do not cause color problems during crystallization which sometimes is a problem with
10 the aromatic ketones.

In one embodiment of the process of our invention, a crude polyester color concentrate is prepared and granulated to a very coarse powder which is then heated with a high-boiling solvent, e.g. methyl benzoate, to
15 facilitate dissolution. Upon cooling, crystallization-precipitation occurs and a diluent such as acetone usually is needed to permit stirring. Filtration gives a finely-divided powder which may require washing or reslurrying to remove the crystallization solvent and
20 low molecular weight oligomeric material.

In another variation of the dissolution-crystallization-precipitation process, crystallization can occur as an integral part of the polyester color concentrate manufacturing process wherein a high-boiling solvent crystallization solvent is added to a melt of
25 the concentrate to obtain a solution of the color concentrate which then may be obtained as a powder by precipitation. The polyester color concentrate powder is thus obtained in a purified form without the need of
30 a granulation step by a means which may be used in conjunction with batch processing. The solvent used in this embodiment normally should have a boiling point of at least 120°C, preferably in the range of about 150 to

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275°C. Examples of such high-boiling inert solvents include lower alkyl, e.g., alkyl of up to about 4 carbon atoms, esters of aromatic mono- and di-carboxylic acids such as methyl benzoate, butyl benzoate, dimethyl 5 phthalate; glycol esters, e.g., ethylene glycol diacetate; aromatic ethers such as diphenyl oxide; alkanoyl benzenes, such as acetophenone; and glycol ethers.

The dissolution-crystallization-precipitation 10 procedure alters the morphology of the amorphous and partially-crystalline polyester color concentrates in a number of respects. X-Ray diffraction analysis of the colored semicrystalline powders shows a marked increase in the crystallinity of the polyester and, while the 15 amorphous polyester concentrates do not exhibit a melting temperature, the microcrystalline concentrates usually (almost always) exhibit a melting temperature by DSC. Although the weight average molecular weight (M_w) may either increase or not be changed by the 20 dissolution-crystallization-precipitation procedure, the number average molecular weight (M_n) always increases, the magnitude of the increase depending on the degree to which oligomeric material has been removed from the colored semicrystalline polyester powder. The poly- 25 dispersity ratio ($M_w:M_n$) of the colored semicrystalline polyester is always less than that of the polyester concentrate from which it is prepared due to the increase in M_n (even when M_w increases, M_n increases more). Finally, the inherent viscosity of the colored 30 semicrystalline powders normally is slightly higher than that of the corresponding color concentrates.

A multiplicity of colors of semicrystalline polyester powders may be obtained by combining

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individual colors, e.g., subtractive colors such as yellow, magenta and cyan according to known color technology (see N. Ohta, Photographic Science and Engineering, Volume 15, No. 5, Sept.-Oct. 1971, 5 pp. 399-415). In the practice of this invention the colors may be combined at various appropriate stages in the preparation of the semicrystalline powders:

(a) two or more copolymerizable colorants are added to the initial polymerization reaction; upon completion of the polycondensation reaction the colored semicrystalline powder is prepared via the above-mentioned dissolution-crystallization-precipitation procedure;

(b) two or more colored amorphous or partially crystalline color concentrates are combined and then converted to a colored semicrystalline polyester powder via the dissolution-crystallization-precipitation;

(c) two or more colored semicrystalline polyester powders are combined and the dissolution-crystallization-precipitation procedure repeated;

(d) two or more colored semicrystalline polyester powders are physically admixed by using known blending methods.

Further, the polyester compositions of the present invention may possess one or more difunctional colorants or may exist as a mixture of polyester compositions, each possessing one or more difunctional colorants. 30 Also, as well understood by those skilled in the art, conventional additives may be present in the colored semicrystalline polyester powder composition of the present invention. For instance, such additives may include plasticizers, flame retardants, nucleating

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agents, stabilizers, antioxidants or opacifiers such as titanium dioxide.

Our novel process and the powder colorant compositions obtained therefrom are further illustrated by the
5 following examples. The inherent viscosities specified herein are determined at 25°C using 0.5 g of polymer (polyester color concentrate or powder colorant composition) per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetra-chloroethane. The weight average molecular weight (Mw)
10 and number average molecular weight (Mn) values referred to herein are determined by gel permeation chromatography. The melting temperatures are determined by differential scanning calorimetry on the first and/or
15 second heating cycle at a scanning rate of 20°C per minute and are reported as the peaks of the transitions.

EXPERIMENTAL SECTION

EXAMPLE 1

20 The following materials are placed in a 500 mL, three-necked, round-bottom flask:

110.4 g (0.569 mol) dimethyl terephthalate

70.5 g (1.138 mol) ethylene glycol

0.0119 g Ti from a n-butanol solution of titanium
25 isopropoxide

12.07 g (0.0215 mol) N,N'-bis-(2,2-dimethyl-3-hydroxypropyl)-3,4,9,10-perylene-tetracarboxylic diimide

The flask is equipped with a nitrogen inlet, stirrer,
30 vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 75 minutes. Over the next 30 minutes the temperature is

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increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 45 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum is relieved with nitrogen and methyl benzoate (175 mL) is added slowly. The mixture is stirred to solution over about 5 10 minutes with the flask still in the metal bath. The heat is then removed and stirring continued. Crystallization begins to occur at about 115°C. At 50°C, 10 acetone (150 mL) is added to facilitate stirring. The diluted slurry is stirred for about 30 minutes, 15 filtered and the cake washed three times with acetone and dried. The resulting dark red polyester contains 10.1 weight percent of the perylene colorant residue, has an inherent viscosity of 0.44, a weight average molecular weight of 43,741, a number average molecular weight of 17,837 and a polydispersity value of 2.45. 20 The yield of powder is 111 g.

EXAMPLE 2

The following materials are placed in a 500 mL, 25 three-necked, round-bottom flask:

80.44 g (0.415 mol) dimethyl terephthalate
67.67 g (0.752 mol) 1,4-butanediol
0.0137 g Ti from a n-butanol solution of titanium tetraisopropoxide
30 41.42 g (0.0866 mol) 1,5-bis(2-carboxyanilino)-anthraquinone

The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and

- 20 -

contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 2 hours. Over the next 30 minutes the temperature is 5 increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and 10 contents at about 275°C for 5 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (125 mL) is added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution 15 is transferred to a 2 L beaker and stirred until crystallization occurs. Acetone:hexane (1:1 by volume) mixture (1.0 L) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake is washed 20 with acetone:hexane (1:1) mixture. The cake is twice reslurried in acetone and then dried in air. The resulting dark red semicrystalline polyester powder, containing 30.16 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.144, a 25 melting temperature of 195°C, a weight average molecular weight of 9,828, a number average molecular weight of 7,037 and a polydispersity value of 1.39. The weight of recovered powder is 127 g.

30 EXAMPLE 3

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

- 21 -

81.38 g (0.419 mol) dimethyl terephthalate
68.00 g (0.755 mol) 1,4-butanediol
0.0139 g Ti from a n-butanol solution of titanium
tetraisopropoxide

5 43.10 g (0.0842 mol) 1,5-bis(o-carboxyphenylthio)-
anthraquinone

The flask is equipped with a nitrogen inlet, stirrer,
vacuum outlet, and condensing flask. The flask and
contents are heated in a Belmont metal bath with a
10 nitrogen sweep over the reaction mixture as the
temperature is increased to 200°C and then to 220°C over
2 hours. Over the next 30 minutes the temperature is
increased to about 240°C and then to about 260°C over
the next 30 minutes. The temperature is quickly raised
15 (over about 10 minutes) to 275°C and a vacuum is applied
until the pressure is reduced to 0.5 mm Hg. The poly-
condensation is completed by heating the flask and
contents at about 275°C for 5 minutes under a pressure
of 0.1 to 0.5 mm Hg. The vacuum is then relieved with
20 nitrogen and methyl benzoate (125 mL) is added slowly
and stirred to solution over about 10 minutes with the
flask still in the metal bath. The resulting solution
is transferred to a 2 L beaker and stirred until
crystallization occurs. Acetone:hexane (1:1 by volume)
25 mixture (1.0 L) is added slowly with stirring to dilute
the slurry and keep it stirrable. The diluted slurry is
stirred for 30 minutes, filtered and the cake is washed
with acetone:hexane (1:1) mixture. The cake is twice
reslurried in acetone and then dried in air. The
30 resulting yellow semicrystalline polyester powder,
containing 30.79 weight percent of the anthraquinone
colorant residue, has an inherent viscosity of 0.12, a
melting temperature of 178°C, a weight average molecular

- 22 -

weight of 8,500, a number average molecular weight of 6,477 and a polydispersity value of 1.31. The weight of recovered powder is 122 g.

5 EXAMPLE 4

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

58.20 g (0.30 mol) dimethyl terephthalate

40.50 g (0.45 mol) 1,4-butanediol

10 0.0025 g Ti from a n-butanol solution of titanium tetraisopropoxide

22.0 g (0.029 mol) blue anthraquinone colorant having the formula:

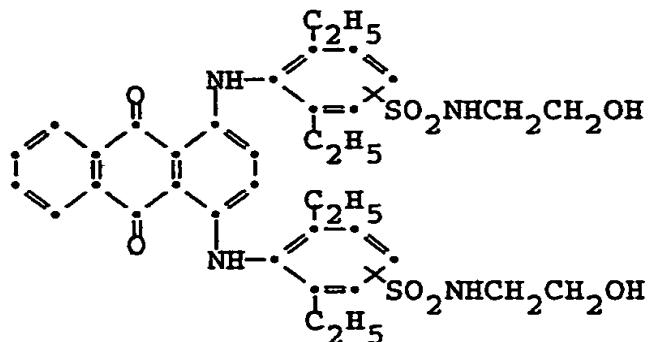
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The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200° and then to 220° over 2 hours. Over the next 30 minutes the temperature is increased to about 240° and then to about 260° over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275° and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and

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- 23 -

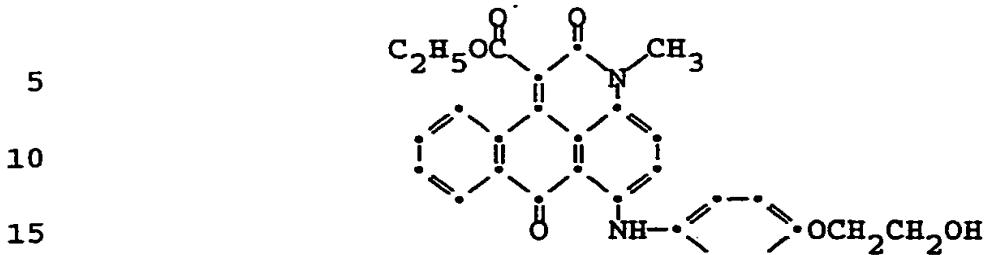
contents at about 275° for 5 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (100 mL) is added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs. Hexane (700 mL) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake is washed with hexane three times and then dried in air. The resulting dark blue semicrystalline polyester powder, containing 25.76 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.103, a melting temperature of 182°C, a weight average molecular weight of 4,181, a number average molecular weight of 1,855 and a polydispersity value of 2.25. The weight of recovered powder is 74.4 g.

20 EXAMPLE 5

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

64.22 g (0.331 mol) dimethyl terephthalate
48.89 g ((0.543 mol) 1,4-butanediol
25 0.0099 g Ti from a n-butanol solution of titanium
tetraisopropoxide
30.0 g (0.0619 mol) red anthrapyridone colorant
having the formula

- 24 -



20 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 2 hours. Over the next 30 minutes the temperature is increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The poly-30 condensation is completed by heating the flask and contents at about 275°C for 5 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (80 mL) is added slowly and stirred to solution over about 10 minutes with the 35 flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs. Acetone (1.0 L) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 40 minutes, filtered and the cake is washed with acetone. The cake is twice reslurried in acetone and then dried in air. The resulting dark red semicrystalline polyester powder, containing 29.99 weight percent of the anthrapyridone colorant residue, has an inherent viscosity of 0.134, a melting temperature of 199°C, a weight

- 25 -

average molecular weight of 7,531, a number average molecular weight of 5,258 and a polydispersity value of 1.43. The weight of recovered powder is 91.2 g.

5 EXAMPLE 6

The following materials re placed in a 500 mL, three-necked, round-bottom flask:

97.00 g (0.50 mol) dimethyl terephthalate

67.50 g (0.75 mol) 1,4-butanediol

10 0.0115 g Ti from a n-butanol solution of titanium tetraisopropoxide

6.0 g (.0106 mol) N,N'-bis-(2,2-dimethyl-3-hydroxy-propyl)-3,4,9,10-perylenetetracarboxylic diimide

15 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 225°C over 20 2 hours. Over the next 50 minutes the temperature is increased to about 255°C. The temperature is quickly raised (over about 25 minutes) to 270°C and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and 25 contents at about 270°C for 15 minutes under a pressure of 0.1 to 0.5 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (125 mL) is added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution 30 is transferred to a 2 L beaker and stirred until crystallization occurs. Acetone (700 mL) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30

- 26 -

minutes, filtered and the cake is washed with acetone. The cake is twice reslurried in acetone and then dried in air. The resulting dark red semicrystalline poly-ester powder, containing 5.21 weight percent of the perylene colorant residue, has an inherent viscosity of 0.418, a melting temperature of 224°C, a weight average molecular weight of 40,954, a number average molecular weight of 18,337 and a polydispersity value of 2.23. The weight of recovered powder is 110 g.

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EXAMPLE 7

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

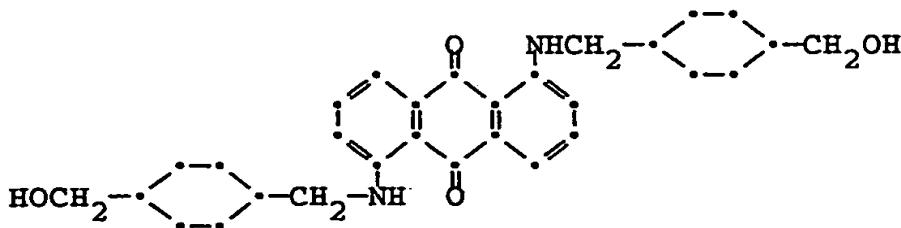
15 75.44 g (0.388 mol) dimethyl terephthalate
 52.50 g (0.583 mol) 1,4-butanediol
 0.0115 g Ti from a n-butanol solution of titanium
 tetraisopropoxide
 36.10 g (0.0736 mol) red anthraquinone colorant
 having the formula:

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40 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 225°C over 2.5 hours. A vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 225°C for 1

- 27 -

hour under a pressure of 0.1 to 0.5 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (125 mL) is added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The 5 resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs. Hexane (700 mL) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake is washed with hexane. 10 The cake is twice reslurried in hexane and then dried in air. The resulting dark red semicrystalline polyester powder, containing 31.38 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.397, a melting temperature of 188°C, a weight average 15 molecular weight of 21,296, a number average molecular weight of 12,060 and a polydispersity value of 1.76. The yield of powder is 85.3 g.

EXAMPLE 8

20 The following materials are placed in a 500 mL, three-necked, round-bottom flask:
135.80 g (0.70 mol) dimethyl terephthalate
94.50 g (1.05 mol) 1,4-butanediol
0.0208 g Ti from a n-butanol solution of titanium 25 tetrakisopropoxide
62.0 g (0.083 mol) blue anthraquinone colorant used in Example 4
The flask is equipped with a nitrogen inlet, stirrer, 30 vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 225°C over 2.5 hours. A vacuum is applied until the pressure is

- 28 -

reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 225°C for 1 hour under a pressure of 0.1 to 0.5 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (125
5 mL) is added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs. Hexane (800 mL) is added slowly with stirring to dilute the slurry and
10 keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake is washed with hexane. The cake is twice reslurried in hexane and then dried in air. The resulting dark blue semicrystalline polyester powder, containing 29.72 weight percent of the anthra-
15 quinone colorant residue, has an inherent viscosity of 0.167, a melting temperature of 182°C, a weight average molecular weight of 8,520, a number average molecular weight of 5,372 and a polydispersity value of 1.59. The yield of powder is 199 g.

20

PREPARATION 1

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

25

135.8 g (0.70 mol) dimethyl terephthalate

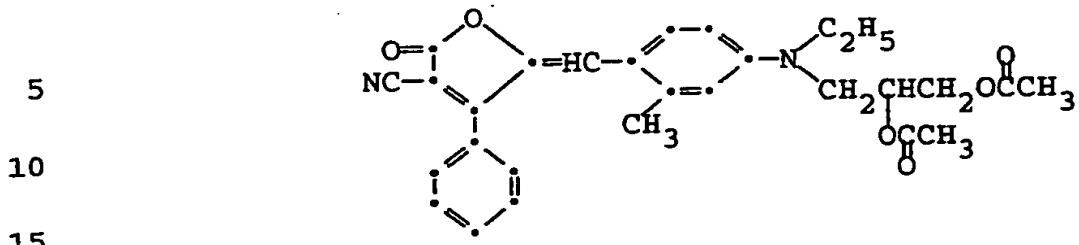
94.6 g (0.91 mol) 2,2-dimethyl-1,3-propanediol

0.0170 g Ti from a n-butanol solution of
titanium tetraisopropoxide

11.73 g (0.024 mol) red methine colorant having
the structure

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The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 30 minutes. Over the next 30 minutes the temperature is increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C. With a stream of nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to about 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 45 minutes under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from the metal bath and is allowed to cool while the polymer solidifies. The resulting high molecular weight red polyester, containing 7.0 weight percent of the methine colorant residue, has an inherent viscosity of 0.57, no melting temperature, a weight average molecular weight of 45,428, a number average molecular weight of 9,349 and a polydispersity value of 4.86.

40 EXAMPLE 9

A portion (50.0 g) of the amorphous color concentrate prepared in PREPARATION 1 is granulated using a Wiley mill and added portionwise to toluene (200 mL) stirred in an explosion-proof Waring blender. After

- 30 -

complete addition, stirring is continued at full speed for about 20 minutes and with the temperature rising to about 80°C. Additional toluene is added to rinse down the walls of the blender container and the mixture 5 allowed to stand overnight to produce solid semicrystalline material. The volume of the mixture is doubled by the addition of acetone. The solid product is collected by filtration and then reslurried four times in acetone by stirring in the Waring blender followed by filtration 10 after each reslurry. After drying in air the red semicrystalline polyester powder weighs 46.0 g, and has an inherent viscosity of 0.58, a weight average molecular weight of 45,167, a number average molecular weight of 13,919 and a polydispersity value of 3.24.

15 The above procedure for crystallization of the poly(2,2-dimethyl-1,3-propanediyl terephthalate) color concentrates is used, with minor modifications, in Examples 10, 11, 12, 13, 14, 15 and 16. Depending upon the solubility of the amorphous color concentrate, 20 stirring is usually continued at full speed for 20-30 minutes or until solution occurs or until the temperature approaches the boiling point of toluene.

EXAMPLE 10

25 The following materials are placed in a 500 mL, three-necked, round-bottom flask:

129.2 g (0.666 mol) dimethyl terephthalate
94.6 g (0.91 mol) 2,2-dimethyl-1,3-propanediol
0.01744 g Ti from a n-butanol solution of
30 titanium tetraisopropoxide
16.4 g (0.0343 m) 1,5-bis(2-carboxyanilino)-anthraquinone

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The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the
5 temperature is increased to 200°C and then to 220°C over 30 minutes. Over the next 20 minutes the temperature is increased to about 240°C and then to about 260°C over the next 15 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C. With a stream of
10 nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to about 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 1 hour under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from
15 the metal bath and is allowed to cool while the polymer solidifies. The resulting high molecular weight, red polyester, containing 9.39 weight percent of the anthra-quinone colorant residue, has an inherent viscosity of 0.53, no melting temperature, a weight average molecular
20 weight of 33,986, a number average molecular weight of 9,805 and a polydispersity value of 3.47.

A portion (50.0 g) of the amorphous color concentrate is converted into a colored semicrystalline polyester powder using the general procedure described
25 in Example 9. The yield is 45.3 g of red powder having an inherent viscosity of 0.55, a melting temperature of 138°C, a weight average molecular weight of 44,436, a number average molecular weight of 16,591 and a polydispersity value of 2.67.

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EXAMPLE 11

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

- 32 -

135.80 g (0.70 mol) dimethyl terephthalate
94.6 g (0.91 mol) 2,2-dimethyl-1,3-propanediol
0.01763 g Ti from a n-butanol solution of
titanium tetraisopropoxide

5 16.0 g (0.0355 mol) 1,4-bis[4-(2-hydroxyethyl)-
anilino]anthraquinone

The flask is equipped with a nitrogen inlet, stirrer,
vacuum outlet, and condensing flask. The flask and
contents are heated in a Belmont metal bath with a
10 nitrogen sweep over the reaction mixture as the
temperature is increased to 200°C and then to 220°C over
90 minutes. Over the next 20 minutes the temperature is
increased to about 240°C and then to about 260°C over
the next 15 minutes. The temperature is quickly raised
15 (over about 10 minutes) to 275°C. With a stream of
nitrogen bleeding into the system a vacuum is applied
until the pressure is reduced to 0.5 mm Hg. The poly-
condensation is completed by heating the flask and
contents at about 275°C for about 1 hour under a
20 pressure of 0.1 to 0.5 mm Hg. The flask is removed from
the metal bath and is allowed to cool while the polymer
solidifies. The resulting high molecular weight,
greenish-blue polyester, containing 9.08 weight percent
of the anthraquinone colorant residue, has an inherent
25 viscosity of 0.49, no melting temperature, a weight
average molecular weight of 38,584, a number average
molecular weight of 17,769 and a polydispersity value of
2.17.

A portion (50 g) of the amorphous color concentrate
30 is crystallized using the general described in Example 9
to produce a greenish-blue semicrystalline polyester
powder (44.8 g) having an inherent viscosity of 0.50, a
melting temperature of 138°C, a weight average molecular

- 33 -

weight of 45,185, a number average molecular weight of 17,562 and a polydispersity value of 2.57.

EXAMPLE 12

5 The following materials are placed in a 500 mL, three-necked, round-bottom flask:

135.80 g (0.70 mol) dimethyl terephthalate

94.60 g (0.91 mol) 2,2-dimethyl-1,3-propanediol

0.01762 g Ti from a n-butanol solution of

10 titanium tetraisopropoxide

16.0 g (0.0314 mol) 1,4-bis[4-(2-hydroxyethoxy)-anilino]anthraquinone

The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 30 minutes. Over the next 20 minutes the temperature is increased to about 240°C and then to about 260°C over the next 15 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C. With a stream of nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to about 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 1 hour under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from the metal bath and is allowed to cool while the polymer solidifies. The resulting high molecular weight polyester, containing 9.08 weight percent of the greenish-blue colorant residue, has an inherent viscosity of 0.71, no melting temperature, a weight average molecular weight of 49,918, a number average molecular weight of 23,654 and a polydispersity value of 2.1.

A portion (50.0 g) of the amorphous color concentrate is converted into a colored semicrystalline polyester powder using the general procedure described in Example 9. The yield is 45.6 g of a greenish-blue 5 powder which has a melting temperature of 137°C, an inherent viscosity of 0.72, a weight average molecular weight of 50,959, a number average molecular weight of 30,849 and a polydispersity of 1.44.

10 EXAMPLE 13

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

131.3 g (0.677 mol) dimethyl terephthalate
145.6 g (1.40 mol) 2,2-dimethyl-1,3-propanediol
15 0.01638 g Ti from a n-butanol solution of
titanium tetraisopropoxide
11.73 g (0.0229 m) 1,5-bis(2-carboxyphenylthio)-
anthraquinone

The flask is equipped with a nitrogen inlet, stirrer, 20 vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 30 minutes. Over the next 15 minutes the temperature is 25 increased to about 240°C and then to about 260°C over the next 15 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C. With a stream of nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The poly- 30 condensation is completed by heating the flask and contents at about 275°C for about 1.25 hours under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from the metal bath and is allowed to cool while the polymer

- 35 -

solidifies. The resulting high molecular weight yellow polyester, containing 7.16 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.57, no melting temperature, a weight average molecular weight of 36,032, a number average molecular weight of 10,391 and a polydispersity value of 3.47. A portion (50 g) of the amorphous polymer is crystallized as in Example 9 to yield 44.3 g of yellow semicrystalline polyester powder.

10

EXAMPLE 14

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

15 131.3 g (0.677 mol) dimethyl terephthalate
 145.6 g (1.40 mol) 2,2-dimethyl-1,3-propanediol
 0.01638 g Ti from a n-butanol solution of
 titanium tetraisopropoxide
 11.73 g (0.0245 m) 1,5-bis-(2-carboxyanilino)-
 anthraquinone

20 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over
25 30 minutes. Over the next 20 minutes the temperature is increased to about 240°C and then to about 260°C over the next 15 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C. With a stream of nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The poly-
30 condensation is completed by heating the flask and contents at about 275°C for about 1.25 hours under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from

- 36 -

the metal bath and is allowed to cool while the polymer solidifies. The resulting high molecular weight red polyester, containing 7.16 weight percent of the anthraquinone colorant residue, has an inherent 5 viscosity of 0.60, no melting temperature, a weight average molecular weight of 35,420, a number average molecular weight of 10,175 and a polydispersity value of 3.48.

10 A portion (50.0 g) of the amorphous polymer is crystallized according to the general procedure of Example 9 to yield 45.2 g of red semicrystalline polyester powder.

EXAMPLE 15

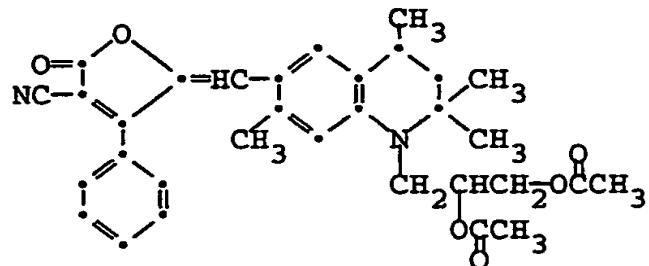
15 The following materials are placed in a 500 mL, three-necked, round-bottom flask:

135.8 g (0.70 mol) dimethyl terephthalate

145.6 g (1.40 mol) 2,2-dimethyl-1,3-propanediol

0.01638 g Ti from a n-butanol solution of
20 titanium tetraisopropoxide

11.73 g (0.0216 m) methine colorant having the
structure:



The flask is equipped with a nitrogen inlet, stirrer, 45 vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the

- 37 -

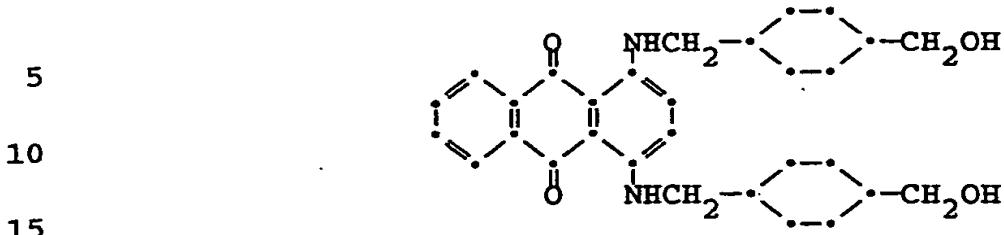
temperature is increased to 200°C and then to 220°C over 30 minutes. Over the next 20 minutes the temperature is increased to about 240°C and then to about 260°C over the next 15 minutes. The temperature is quickly raised 5 (over about 10 minutes) to 275°C. With a stream of nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 1.25 hours under a 10 pressure of 0.1 to 0.5 mm Hg. The flask is removed from the metal bath and is allowed to cool while the polymer solidifies. The resulting high molecular weight red polyester, containing 7.16 weight percent of the methine colorant residue, has an inherent viscosity of 0.56, no 15 melting temperature, a weight average molecular weight of 37,995, a number average molecular weight of 9,014 and a polydispersity value of 4.2.

A portion (50 g) of the amorphous polymer is crystallized as in Example 9 to yield 45.4 g of bright 20 magenta, semicrystalline, polyester powder.

EXAMPLE 16

The following materials are placed in a 500 mL, three-necked, round-bottom flask:

25 135.8 g (0.70 mol) dimethyl terephthalate
145.6 g (1.40 mol) 2,2-dimethyl-1,3-propanediol
0.01638 g Ti from a n-butanol solution of
titanium tetraisopropoxide
30 11.73 g (0.0239 mol) blue anthraquinone
colorant having the structure:



The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C, and then to 220°C over 30 minutes. Over the next 20 minutes the temperature is increased to about 240°C and then to about 260°C over the next 15 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C. With a stream of nitrogen bleeding into the system a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 1.25 hours under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from the metal bath and is allowed to cool while the polymer solidifies. The resulting high molecular weight dark blue polyester, containing 7.16 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.524, no melting temperature, a weight average molecular weight of 33,811, a number average molecular weight of 9,708 and a polydispersity value of 3.48.

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PREPARATION 2

The following materials are placed in a 500-mL, three-necked, round-bottom flask:

133.6 g (0.689 mol) dimethyl terephthalate

85.5 g (1.380 mol) ethylene glycol

0.0178 g Ti from a n-butanol solution of
titanium tetraisopropoxide

54.0 g (0.132 mol) 1,5-bis[(3-hydroxy-2,2-dimethylpropyl)amino]anthraquinone

10 The flask is equipped with a nitrogen inlet, stirrer,
vacuum outlet, and condensing flask. The flask and
contents are heated in a Belmont metal bath with a
nitrogen sweep over the reaction mixture as the
temperature is increased to 200°C and then to 220°C over
15 75 minutes. Over the next 30 minutes the temperature is
increased to about 240°C and then to about 260°C over
the next 30 minutes. The temperature is quickly raised
(over about 10 minutes) to 275°C and a vacuum is
applied until the pressure is reduced to 0.5 mm Hg. The
polycondensation is completed by heating the flask and
20 contents at about 275°C for about 45 to 60 minutes under
a pressure of 0.1 to 0.5 mm Hg. The flask is removed
from the metal bath and is allowed to cool while the
polymer solidifies. The resulting dark red polyester,
25 containing 30.3 weight percent of the anthraquinone
colorant residue, has an inherent viscosity of 0.49.

PREPARATION 3

The following materials are placed in a 500-mL, round-bottom flask:

105.6 (6.76 mol) dimethyl

135.8 g (0.70 mol) dimethyl terephthalate

94.6 g (0.91 mol) 2,2-dimethyl-1,3-propanedioi

- 40 -

0.0177 g Ti from a n-butanol solution of
titanium tetraisopropoxide

18.0 g (0.044 mol) 1,5-bis[(3-hydroxy-2,2-di-
methylpropyl)amino]anthraquinone

5 The flask is equipped with a nitrogen inlet, stirrer,
vacuum outlet, and condensing flask. The flask and
contents are heated in a Belmont metal bath with a
nitrogen sweep over the reaction mixture as the
temperature is increased to 200°C and then to 220°C over
10 90 minutes. Over the next 30 minutes the temperature is
increased to about 240°C and then to about 260°C over
the next 30 minutes. The temperature is quickly raised
(over about 10 minutes) to 275°C and a vacuum is
15 applied until the pressure is reduced to 0.5 mm Hg. The
polycondensation is completed by heating the flask and
contents at about 275°C for 75 minutes under a pressure
of 0.1 to 0.5 mm Hg. The flask is removed from the
metal bath and is allowed to cool while the polymer
solidifies. The resulting dark red polyester,
20 containing 30.3 weight percent of the anthraquinone
colorant residue, has an inherent viscosity of 0.56, no
melting temperature, a weight average molecular weight
of 39,000, a number average molecular weight of 20,000
and a polydispersity value of 1.94.

25

EXAMPLE 17

A portion (25.0 g) of the amorphous polyester color
concentrate prepared in PREPARATION 3 is granulated
using a Wiley mill and dissolved in methylene chloride
30 (200 mL) at about 25°C with stirring. Ethyl acetate
(200 mL) is added and the methylene chloride is removed
by distillation. The mixture is stirred for about 12 to
15 hours (usually overnight) at about 25°C during which

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time the colored semicrystalline powder separates. Acetone (200 mL) is added with stirring and the solid is collected by filtration and slurried in acetone (200 mL) and filtered four times to remove oligomers from the 5 product which after drying weighs 23.6 g. The colored semicrystalline powder thus prepared has an inherent viscosity of 0.58, a melting temperature of 144°C, a weight average molecular weight of 38,000, a number average molecular weight of 25,000 and a polydispersity 10 value of 1.52. The accountability of the anthraquinone colorant compound is 93% as determined by visual spectroscopy and a comparison of the absorbance of a methylene chloride solution of 1,5-bis[(3-hydroxy-2,2-dimethylpropyl)amino]anthraquinone with the absorbance 15 of a methylene chloride solution of the microcrystalline color concentrate. The comparison shows no shift in absorbance indicating that the colorant is not decomposed during the synthesis of the polyester.

20 EXAMPLE 18

The procedure of PREPARATION 3 is repeated using:
108.6 g (0.560 mol) dimethyl terephthalate
75.7 g (0.728 mol) 2,2-dimethyl-1,3-propanediol
0.0170 g Ti from a n-butanol solution of
25 titanium tetraisopropoxide
52.0 g (0.44 mol) 1,5-bis[(3-hydroxy-2,2-di-methylpropyl)amino]anthraquinone

The dark red polyester color concentrate contains 30.6 weight percent of the residue of 1,5-bis[(3-hydroxy-2,2-dimethylpropyl)amino]anthraquinone and has an inherent viscosity of 0.47, a weight average molecular weight of 31,000, a number average molecular weight of 17,000 and a polydispersity value of 1.84.

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The procedure described in Example 17 is repeated precisely using 25.0 g of the color concentrate to give 22.4 g of dark red, semicrystalline powder having an inherent viscosity of 0.49, a weight average molecular weight of 35,000, a number average molecular weight of 25,000 and a polydispersity value of 1.42. The accountability of the anthraquinone colorant by visual spectroscopy is 91.1%.

10 EXAMPLE 19

A portion (57.2 g) of the color concentrate prepared in Example 18 is granulated and partially dissolved in boiling ethyl acetate (480 mL) by stirring. The mixture is cooled with stirring to 25°C at a rate of less than 1°C per minute. Stirring is stopped and the color concentrate is allowed to precipitate and undergo solvent-induced crystallization for about 15 hours. The dark red crystalline solid is separated by filtration and slurried in acetone (300 mL) three or four times to remove any low molecular weight oligomers from the product. After the last filtration, the solid is dried to give 45.1 g of colored semicrystalline powder having a melting temperature of 122°C, a weight average molecular weight of 36,122, a number average molecular weight of 26,224 and a polydispersity value of 1.38. Color accountability, determined as described in Example 17, is 93%.

EXAMPLE 20

30 The procedure of PREPARATION 3 is repeated using:

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84.1 g (0.43 mol) dimethyl terephthalate
58.6 g (0.56 mol) 2,2-dimethyl-1,3-propanediol
0.0165 g Ti from a n-butanol solution of
titanium tetraisopropoxide
5 85.1 g (0.21 mol) 1,5-bis[(3-hydroxy-2,2-di-
methylpropyl)amino]anthraquinone

The extremely dark red polyester color concentrate
contains 51.6 weight percent of the residue of 1,5-bis-
[(3-hydroxy-2,2-dimethylpropyl)amino]anthraquinone and
10 has an inherent viscosity of 0.36.

The procedure described in Example 17 is repeated
precisely using 25.0 g of the color concentrate to give
22.9 g of very dark red, semicrystalline powder.

15 EXAMPLE 21

A portion (75.0 g) of the color concentrate
prepared in Example 20 is ground and crystallized from
ethyl acetate (500 mL) as described in Example 19 to
obtain 58.8 g of very dark red crystalline color
20 concentrate with an anthraquinone colorant account-
ability of 93%.

EXAMPLE 22

The following materials are placed in a 500-mL
25 three-necked, round-bottom flask:

145.50 g (0.750 mol) dimethyl terephthalate
101.25 g (1.125 mol) 1,4-butanediol
0.0214 g Ti from a n-butanol solution of
titanium tetraisopropoxide
30 63.00 g (0.044 mol) 1,5-bis[(3-hydroxy-2,2-di-
methylpropyl)amino]anthraquinone

The flask is equipped with a nitrogen inlet, stirrer,
vacuum outlet, and condensing flask. The flask and

contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C. The mixture is heated at 200°C for 1.75 hours and then the temperature 5 is raised to and maintained at 225°C over a period of 2.25 hours. The nitrogen sweep is then stopped and vacuum is applied to lower the pressure to about 0.5 to 1.0 mm Hg. The polycondensation is completed by heating the flask and contents at about 225°C for 1 hour under a 10 pressure of 0.5 to 1.0 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (125 mL) is added slowly and stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and 15 stirred until crystallization occurs. Hexane (700 mL) is added slowly with stirring to dilute the slurry and keep it stirrable. (Acetone, which removes more oligomeric material, also may be used.) The diluted slurry is stirred for 30 minutes, filtered and the cake 20 is washed with hexane. The cake is twice reslurried in hexane and then dried in a vacuum oven. The resulting dark red semicrystalline polyester powder, containing 29.42 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.202, a melting 25 temperature of 175°C, a glass transition temperature of 66°C, a weight average molecular weight of 12,646, a number average molecular weight of 8,359 and a polydispersity value of 1.51. Reslurrying the powder twice in acetone increases the non-extractability of 30 color and raises the inherent viscosity to 0.26.

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EXAMPLE 23

The procedure described in Example 22 is repeated except that the reaction mixture is heated at 200°C for 1.75 hours and then the temperature is raised to 220°C over 1.25 hours, then to 240°C over 1.25 hours and finally to 270°C over 1.25 hours. Vacuum is applied to lower the pressure to about 0.5 to 1.0 mm Hg and polycondensation is completed by heating the flask and contents at about 270°C for 22 minutes under a pressure of 0.5 to 1.0 mm Hg. The vacuum is then relieved with nitrogen and methyl benzoate (125 mL) is added slowly and stirred to solution over about 50 minutes with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs. Acetone (1 L) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake is slurried in hexane (1 L). The cake is again slurried in acetone and hexane and then dried in air to yield 212.89 g (99.40% of theory) colored powder. The dark red polyester powder, containing 29.42 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.190, a melting temperature of 172°C, a glass transition temperature of 54°C, a weight average molecular weight of 12,806, a number average molecular weight of 8,903 and a polydispersity value of 1.44.

EXAMPLE 24

The following materials are placed in a 500-mL, three-necked, round-bottom flask:

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91.0 g (0.469 mol) dimethyl terephthalate

63.3 g (0.704 mol) 1,4-butanediol

0.01343 g Ti from a n-butanol solution of
titanium tetraisopropoxide

5 40.0 g (0.0976 mol) 1,5-bis[(3-hydroxy-2,2-di-
methylpropyl)amino]anthraquinone

The flask is equipped with a nitrogen inlet, stirrer,
vacuum outlet, and condensing flask. The flask and
contents are heated in a Belmont metal bath with a
10 nitrogen sweep over the reaction mixture as the
temperature is increased to 200°C and then to 220°C over
2 hours. Over the next 30 minutes the temperature is
increased to about 240°C and then to about 260°C over
the next 30 minutes. The temperature is quickly raised
15 (over about 10 minutes) to 275°C and a vacuum is
applied until the pressure is reduced to 0.5 mm Hg. The
polycondensation is completed by heating the flask and
contents at about 275°C for 45 minutes under a pressure
of 0.1 to 0.5 mm Hg. The vacuum is then relieved with
20 nitrogen and methyl benzoate (125 mL) is added slowly
and stirred to solution over about 10 minutes with the
flask still in the metal bath. The resulting solution
is transferred to a 2 L beaker and stirred until
crystallization occurs. Acetone (500 mL) is added
25 slowly with stirring to dilute the slurry and keep it
stirrable. The diluted slurry is stirred for 30
minutes, filtered and the cake is washed with acetone.
The cake is twice reslurried in acetone and then dried
in air. The resulting dark red semicrystalline polyester
30 powder, containing 29.77 weight percent of the
anthraquinone colorant residue, has an inherent
viscosity of 0.485, a melting temperature of 182°C, a
weight average molecular weight of 36,927, a number

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average molecular weight of 23,685 and a polydispersity value of 1.59.

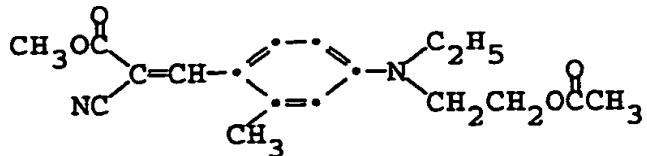
PREPARATION 4

5 The following materials are placed in a 500-mL three-necked, round-bottom flask:
 125.1 g (0.645 mol) dimethyl terephthalate
 94.6 g (0.91 mol) 2,2-dimethyl-1,3-propanediol
 0.01864 g Ti from a n-butanol solution of
 10 titanium tetraisopropoxide
 36.3 g (0.11 mol) methine colorant having the structure:

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The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 90 minutes. Over the next 30 minutes the temperature is increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C with a stream of nitrogen bleeding into the system and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 1.25 hours under a pressure of 0.1 to 0.5 mm Hg. The flask is removed from the metal bath and is allowed to cool while the

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polymer solidifies. The resulting high molecular weight yellow polyester, containing 19.76 weight percent of the methine colorant residue, has an inherent viscosity of 0.30, no melting temperature, a weight average 5 molecular weight of 21,691, a number average molecular weight of 13,366 and a polydispersity value of 1.63.

EXAMPLE 25

A portion (25.0 g) of the amorphous polyester color 10 concentrate prepared in PREPARATION 4 is granulated using a Wiley mill and dissolved in methylene chloride (200 mL) at about 25°C with stirring. Ethyl acetate (200 mL) is added and the methylene chloride is removed by distillation. The mixture is stirred for about 12 to 15 hours (usually overnight) at about 25°C during which time the colored semicrystalline powder separates. The solid is collected by filtration and reslurried in acetone (200 mL each time) and filtered four times to remove oligomers from the product which after drying 20 weighs 20.0 g. The colored semicrystalline powder thus prepared has an inherent viscosity of 0.35, a melting temperature of 134°C, a weight average molecular weight of 23,793, a number average molecular weight of 17,323 and a polydispersity value of 1.37. The total 25 accountability of the methine colorant compound is 93% as determined by visual spectroscopy and a comparison of the absorbance of a methylene chloride solution of the starting methine colorant reactant with the absorbance of a methylene chloride solution of the color 30 concentrate. The comparison shows no shift in absorbance indicating that the colorant is not decomposed during the synthesis of the polyester.

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EXAMPLE 26

The following materials are placed in a 500-mL, three-necked, round-bottom flask:

97.0 g (0.50 mol) dimethyl terephthalate

5 62.0 g (1.00 mol) ethylene glycol

0.0120 g Ti from a n-butanol solution of
titanium tetraisopropoxide

36.0 g (0.109 mol) methine colorant used in

PREPARATION 4

10 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over 15 75 minutes. Over the next 30 minutes the temperature is increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The 20 polycondensation is completed by heating the flask and contents at about 275°C for about 45 to 60 minutes under a pressure of 0.1 to 0.5 mm Hg. Upon completion of polycondensation, the vacuum is relieved with nitrogen and methyl benzoate (160 mL) is added slowly. The 25 mixture is stirred to solution over about 10 minutes with the flask still in the metal bath. The heat is then removed and stirring continued. Crystallization begins to occur at about 115°C. At 50°C, acetone (150 mL) is added to facilitate stirring. The diluted slurry 30 is stirred for about 30 minutes, filtered and the cake washed three times with acetone and dried. The resulting dark yellow polyester contains 29.9 weight percent of the methine colorant residue, has an inherent

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viscosity of 0.29, a weight average molecular weight of 30,518, a number average molecular weight of 16,889 and a polydispersity value of 1.80. The weight of polyester color concentrate powder recovered is 104.7 g, 86.9% of
5 theory.

EXAMPLE 27

The procedure described in Example 26 is repeated except that upon completion of the polycondensation, the
10 vacuum is relieved with nitrogen and diphenyl oxide (200 mL) is added dropwise and the mixture is stirred to solution. Heating is discontinued and crystallization begins to occur at about 130°C. At about 100°C, acetone (100 mL) is added to facilitate stirring. The diluted
15 slurry is filtered and the cake washed well with acetone and dried in air (yield - 100.5 g). The resulting dark yellow polyester contains 29.9 weight percent of the methine colorant residue, has an inherent viscosity of 0.67, a melting temperature of 176°C, a
20 glass transition temperature of 80°C, a weight average molecular weight of 46,040, a number average molecular weight of 22,502 and a polydispersity value of 2.05.

EXAMPLE 28

25 The following materials are placed in a 500-mL, three-necked, round-bottom flask:

97.0 g (0.50 mol) dimethyl terephthalate
67.5 g (0.75 mol) 1,4-butanediol
0.0142 g Ti from a n-butanol solution of
30 titanium tetraisopropoxide
45.0 g (0.136 mol) methine colorant used in
PREPARATION 4

The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the

5 temperature is increased to 200°C and then to 220°C over 2 hours. Over the next 30 minutes the temperature is increased to about 240°C and then to about 260°C over the next 30 minutes. The temperature is quickly raised (over about 10 minutes) to 275°C and a vacuum is

10 applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 275°C for about 45 minutes under a pressure of 0.1 to 0.5 mm Hg. Upon completion of the polycondensation, the vacuum is relieved with nitrogen

15 and methyl benzoate (125 mL) is added slowly and the mixture is stirred to solution with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs. Acetone (500 mL) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake washed with acetone. The cake is twice reslurried in acetone and then dried in air. The resulting dark yellow semicrystalline polyester powder contains 31.5

20 weight percent of the methine colorant residue, has an inherent viscosity of 0.359, a melting temperature of 185°C, a weight average molecular weight of 29,385, a number average molecular weight of 17,655 and a polydispersity value of 1.66. The weight of the powder

25 recovered is 129.4 g, 90.8% of theory.

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EXAMPLE 29

The following materials are placed in a 500-ml three-necked, round-bottom flask:

PREPARATION 4

10 The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet, and condensing flask. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 220°C over
15 2 hours. Over the next 90 minutes the temperature is increased to about 230°C and a vacuum is applied until the pressure is reduced to 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 230°C for about 8 hours under a pressure of 0.1 to 0.5 mm Hg. The vacuum is relieved with nitrogen and methyl benzoate (200 mL) is added slowly and the mixture is stirred to solution over about 10 minutes with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until
20 crystallization occurs. Hexane (800 mL) is added slowly with stirring to dilute the slurry and keep it stirrable. The diluted slurry is stirred for 30 minutes, filtered and the cake is washed with acetone. The cake is twice reslurried in acetone and the dried in
25 air. The resulting dark yellow semicrystalline polyester powder contains 30.87 weight percent of the methine colorant residue, has an inherent viscosity of 0.550, a melting temperature of 179°C, a weight average
30 molecular weight of 10,000, and a number molecular weight of 2,500.

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molecular weight of 33,707, a number average molecular weight of 19,956 and a polydispersity value of 1.69. The weight of the powder recovered is 213.4 g.

5 EXAMPLE 30

The procedure described in Reference Example 4 is repeated using the following materials:

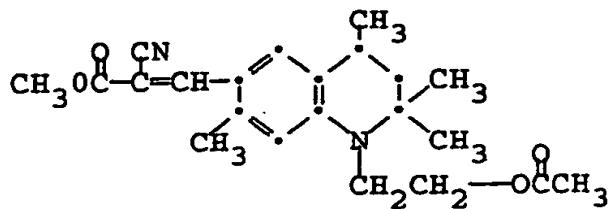
126.5 g (0.652 mol) dimethyl terephthalate

94.6 g (0.91 mol) 2,2-dimethyl-1,3-propanediol

10 0.01864 g Ti from a n-butanol solution of titanium tetraisopropoxide

37.0 g (0.096 mol) methine colorant having the structure:

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The resulting dark yellow polyester contains 19.8 weight percent of the methine colorant residue, has an inherent viscosity of 0.38, no melting temperature, a weight average molecular weight of 27,625, a number average molecular weight of 13,770 and a polydispersity value of 1.78. A portion (25.0 g) of the amorphous color concentrate is crystallized according to the procedure of Example 25 to obtain an essentially theoretical yield of colored semi-crystalline powder having an inherent viscosity of 0.37, a weight average molecular weight of 27,625, a number average molecular weight of 19,130, a polydispersity value of 1.4 and a melting temperature of about 130°C.

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EXAMPLE 31

The following materials are charged to the reactor:

11.90 lbs. (27.8 mol) dimethyl terephthalate
12.47 lbs. (62.8 mol) 1,4-butanediol
5 14.58 g Ti from a n-butanol solution of
titanium tetraisopropoxide
1.50 lbs. (1.42 mol) 1,5-bis(carboxy-
anilino)anthraquinone

The jacketed reactor is equipped with a nitrogen
10 inlet, stirrer, vacuum outlet, and condenser, and is
heated by oil circulating through the jacket. The
reactor is continuously purged with nitrogen while the
contents of the reactor are heated to 180°C over two
hours. The temperature is held for 30 minutes at 180°C,
15 then increased to 200°C over 30 minutes. The tempera-
ture is held for 30 minutes at 200°C, then increased to
220°C over 20 minutes. Over the next 90 minutes the
temperature is increased to 230°C and a vacuum is
applied until the pressure is reduced to 3900 microns
20 Hg. The polycondensation is completed by holding the
reactor contents at 230°C and about 2500 microns Hg
pressure for 15 minutes. The reactor is then
pressurized with nitrogen to extrude the contents of the
reactor into water. The extruded polymer is granulated
25 by grinding in a Wiley mill, then dried under vacuum at
80°C for four hours.

The resulting dark red polyester contains 10.4
weight percent of the anthraquinone colorant residue and
has an inherent viscosity of 0.24. With the gel
30 permeation chromatography detector at 254 nm, the
polyester has a weight average molecular weight of
13,182, a number average molecular weight of 8,856, and
a polydispersity value of 1.49. With the detector at

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546 nm, the weight average molecular weight is 12,855, the number average molecular weight is 8,210, and the polydispersity value is 1.57. The yield of the polyester is 85.4%.

5 A portion (700 g) of the partially-crystalline color concentrate is added to 3500 ml ethylene glycol diacetate in a 5 L round-bottom flask. The mixture is heated to the boiling point of the solvent (188°C) and refluxed for one hour, which dissolves the color
10 concentrate. The solution is cooled to room temperature to precipitate the solid semicrystalline material. The solid product is collected by filtration, washed on the filter with 1400 ml ethylene glycol diacetate, and dried under vacuum at 100°C for 48 hours. The resulting dark
15 red semicrystalline polyester powder contains 9.4 weight percent of the anthraquinone colorant residue, has an inherent viscosity of 0.24, and a melting temperature of 210°C. With the gel permeation chromatography detector at 254 nm, the powder has a weight average molecular
20 weight of 14,080, a number average molecular weight of 10,122, and a polydispersity value of 1.39. With the detector set at 546 nm, the weight average molecular weight is 14,252, the number average molecular weight is 10,823, and the polydispersity value is 1.32. The
25 weight of the powder recovered from the dissolution-crystallization-precipitation process is 675.6 g (96.5% yield). After dispersing a portion of the powder in castor oil by milling on a Hoover muller, the colorant does not bleed into the castor oil. The powder is
30 ground by a Trost TX air impact pulverizer to give an average particle size of 3.9 microns; as measured by the Microtrac particle size analyzer.

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PREPARATION 5

Example 4 above is repeated except the blue colored polymer is not crystallized from methyl benzoate. After the polycondensation step is completed at 275°C, the 5 flask is removed from the metal bath and allowed to cool while the polymer solidifies. The color concentrate is granulated by grinding to a particle size of about 3 mm using a Wiley mill.

10 PREPARATION 6

Example 22 above is repeated, except the red colored polymer is not crystallized from methyl benzoate. After the polycondensation step is completed at 275°C, the 15 flask is removed from the metal bath and allowed to cool while the polymer solidifies. The color concentrate is granulated by grinding to a particle size of about 3 mm using a Wiley mill.

PREPARATION 7

20 Example 29 above is repeated except the yellow colored polymer is not crystallized from methyl benzoate. After the polycondensation reaction is completed at 275°C., the flask is removed from the metal bath and allowed to cool while the polymer solidifies. 25 The color concentrate is granulated by grinding to a particle size of about 3 mm using a Wiley mill.

EXAMPLE 32

The yellow polymeric colorant of Example 29
30 (2.0 g), the red polymeric colorant of Example 22 (3.5 g) and the blue polymeric colorant of Example 4 (4.5 g) are added to a flask which contains methyl benzoate (100 ml). Heating and stirring under nitrogen

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are continued for about 1 hour with the temperature rising to about 200°C. The heat is removed and the solution allowed to cool to room temperature with stirring whereupon the black colored polyester is crystallized. Hexane (100 ml) is added slowly with stirring. The diluted slurry is stirred for 15 min, filtered and the cake washed twice with hexane and air dried. A reddish-black colored semicrystalline powder (9.54 g) is obtained which has an inherent viscosity of 0.158, a melting temperature of 177°C, a weight average molecular weight of 8,714 and a number average molecular weight of 2,636.

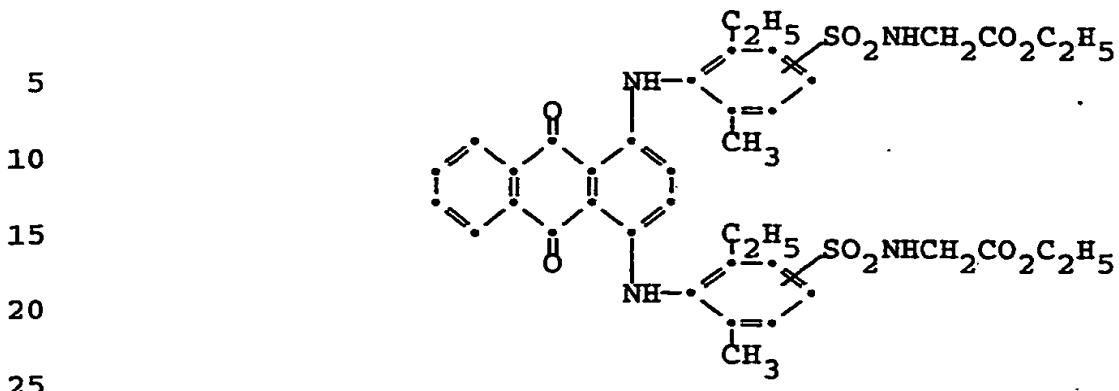
EXAMPLE 33

Example 32 is repeated using the blue polymer of PREPARATION 5 (4.5 g) the red polymer of PREPARATION 6 (3.5 g) and the yellow polymer of PREPARATION 7 (2.0 g). A reddish-black semicrystalline powder is obtained.

EXAMPLE 34

The following materials are placed in a 500-ml three-necked, round-bottom flask:

111.6 g (0.575 mol) dimethyl terephthalate
81.0 g (0.90 mol) 1,4-butanediol
0.0141 g Ti from n-butanol solution of titanium tetraisopropoxide
4.73 g (.00989 mol) red colorant [1,5-bis(o-carboxyanilino)anthraquinone]
4.73 g (.00924 mol) yellow colorant [1,5-bis(o-carboxyphenylthio)anthraquinone]
4.73 g (.00588 mol) blue colorant having the structure



The flask is equipped with a nitrogen inlet, stirrer, vacuum outlet and condensing flask.. The flask and contents are heated in a Belmont metal bath with a nitrogen sweep over the reaction mixture as the temperature is increased to 200°C and then to 225°C over two hours. Over the next hour, the temperature is increased to about 240°C and then to 250°C over the next 15 minutes and a vacuum is applied until the pressure is reduced to about 0.5 mm Hg. The polycondensation is completed by heating the flask and contents at about 250°C for 1 hour. Upon completion of the polycondensation, the vacuum is relieved and methyl benzoate (125 ml) is added slowly and the mixture is stirred to solution with the flask still in the metal bath. The resulting solution is transferred to a 2 L beaker and stirred until crystallization occurs.

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EXAMPLE 35

Example 23 is repeated except finely divided titanium dioxide (TiO_2) is added (2.14 g) along with the reactants. The bright red polyester powder, containing 5 29.42 weight percent of the anthraquinone colorant and 1% of TiO_2 , has an inherent viscosity of 0.146, a melting temperature of 182°C, a glass transition temperature of 37°C, a weight average molecular weight of 8,218, a number average molecular weight 6,235 and a 10 polydispersity value of 1.32. The weight of powder recovered is 198.6 g, 91.8% of the theoretical weight.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the 15 invention.

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CLAIMS

We claim:

1. A semicrystalline powder colorant composition
5 having an average particle size of less than
50 microns comprising a polyester which has been
modified by dissolution-crystallization-
precipitation to impart crystallinity thereto
having copolymerized therein at least 1.0 weight
10 percent, based on the weight of the composition, of
the residue of one or more thermally-stable,
difunctional, colorant compounds.
2. A semicrystalline powder colorant composition
15 according to Claim 1 comprising a normally-
amorphous polyester having an inherent viscosity of
at least 0.2 which has been modified by
dissolution-crystallization-precipitation to impart
crystallinity thereto comprised of:
20 (i) diacid residues comprised of at least
50 mole percent terephthalic and/or
2,6-naphthalenedicarboxylic acid residues;
(ii) diol residues comprised of at least 50 mole
percent of the residue of a diol having the
25 formula:
30
$$\text{HO}-\text{CH}_2-\overset{\text{R}^1}{\underset{\text{R}^2}{\text{C}}} \text{CH}_2-\text{OH}$$
 and
35 wherein R^1 is hydrogen or lower alkyl and R^2
is lower alkyl; and
(iii) at least 5.0 weight percent, based on the
weight of the composition, residues of one

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or more thermally-stable, difunctional, colorant compounds.

3. A semicrystalline powder colorant composition
5 according to Claim 1 having an average particle size of less than 50 microns comprising a normally-amorphous polyester having an inherent viscosity of about 0.2 to 0.8 which has been modified by dissolution-crystallization-precipitation to impart
10 crystallinity thereto comprised of:
 - (i) diacid residues comprised of at least 80 mole percent terephthalic and/or 2,6-naphthalenedicarboxylic acid residues;
 - (ii) diol residues comprised of at least 80 mole percent of the residue of a diol having the formula:
15
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{HO}-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} \\ | \\ \text{CH}_3 \end{array}$$
 and
- 20 25
(iii) at least 5.0 weight percent, based on the weight of the composition, residues of a
30 thermally-stable, difunctional, colorant compound.
4. A semicrystalline powder colorant composition
35 according to Claim 2 wherein component (iii) constitutes about 10 to 40 weight percent of the composition.
5. A semicrystalline powder colorant composition
40 according to Claim 1 having an average particle size of less than 50 microns comprising a

partially-crystalline polyester which had been modified by dissolution-crystallization-precipitation to impart increased crystallinity thereto comprised of:

5 (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues, 2,6-naphthalenedicarboxylic acid residues, 1,3-cyclohexanedicarboxylic acid residues, 1,4-cyclohexanedicarboxylic acid residues
10 or a mixture thereof;

10 (ii) diol residues comprised of at least 50 mole percent of residues having the formula $-O-(CH_2)_p-O-$ wherein p is 2 to 12; and
15 (iii) at least 5.0 weight percent, based on the weight of the composition, residues of one or more thermally-stable, difunctional colorant compounds.

20 6. A semicrystalline powder colorant composition according to Claim 5 comprised of:

20 (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues, 2,6-naphthalenedicarboxylic acid residues, 1,3-cyclohexanedicarboxylic acid residues, 25 1,4-cyclohexanedicarboxylic acid residues or a mixture thereof;
(ii) diol residues comprised of at least 50 mole percent of residues having the formula $-O-(CH_2)_p-O-$ wherein p is 4 to 12; and
30 (iii) at least 5.0 weight percent, based on the weight of the composition, residues of one or more thermally-stable, difunctional, colorant compounds.

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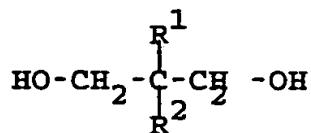
7. A semicrystalline powder colorant composition according to Claim 5 comprising a polyester having an inherent viscosity of at least 0.20 and a melting temperature of at least 110°C comprised of:
 - 5 (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues;
 - (ii) diol residues comprised of at least 80 mole percent of residues of 1,4-butanediol; and
 - (iii) about 10 to 40 weight percent, based on the weight of the composition, residues of one or more thermally-stable, difunctional, colorant compounds.
- 10 8. A semicrystalline powder colorant composition according to Claim 6 wherein component (iii) constitutes about 10 to 40 weight percent of the composition.
- 15 9. A process for the preparation of a semicrystalline powder colorant composition which comprises:
 - 20 (1) dissolving in an inert, organic solvent a polyester color concentrate comprising a polyester having copolymerized therein at least 1.0 weight percent of the residues of at least one thermally-stable, difunctional colorant compound; and
 - (2) precipitating from the solution of step (1) the semicrystalline colorant composition in a finely divided form comprised of particles having an average particle size of less than 25 50 microns.
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10. A process according to Claim 9 wherein dissolution
is performed at a temperature of about 25°C up to
the boiling point of the inert solvent and the
inert solvent is selected from aliphatic chlorides,
5 alkyl carboxylic acid esters having 3 to about 10
carbon atoms and mixtures thereof.

11. A process for the preparation of a semicrystalline
powder colorant composition which comprises:
10 (1) dissolving in an inert, organic solvent
selected from aliphatic chlorides, alkyl
carboxylic acid esters having 3 to about 10
carbon atoms and mixtures thereof an amorphous
polyester color concentrate having an inherent
15 viscosity of at least 0.2 comprising:
(i) diacid residues comprised of at least
50 mole percent terephthalic and/or
2,6-naphthalenedicarboxylic acid
residues;

20 (ii) diol residues comprised of at least
50 mole percent of the residue of a diol
having the formula:



35 wherein R^1 is hydrogen or lower alkyl
and R^2 is lower alkyl; and
(iii) at least 5.0 weight percent, based on
the weight of the composition, residues
of one or more thermally-stable,

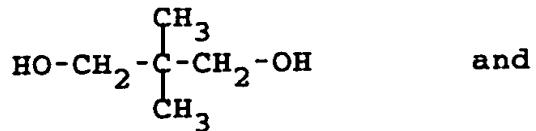
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difunctional, colorant compounds
copolymerized in the polyester; and

5 (2) precipitating from the solution of step (1)
the semicrystalline colorant composition in a
finely divided form consisting of particles
having an average particle size of less than
50 microns.

10 12. A process according to Claim 11 wherein the
amorphous polyester has an inherent viscosity of
about 0.2 to 0.8 and is comprised of:

15 (i) diacid residues comprised of at least
80 mole percent terephthalic and/or
2,6-naphthalenedicarboxylic acid residues;
(ii) diol residues comprised of at least 80 mole
percent of the residue of a diol having the
formula:



30 (iii) about 10 to 40 weight percent, based on the
weight of the composition, residues of a
thermally-stable, difunctional, colorant
compound copolymerized in the polyester.

35 13. A process according to Claim 11 wherein step (1)
comprises dissolving a melt of the partially
crystalline polyester in an inert solvent selected
from lower alkyl esters of aromatic mono- and di-
carboxylic acids.

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14. Process for the preparation of a semicrystalline powder colorant composition which comprises:

(1) dissolving in an inert, organic solvent selected from aliphatic chlorides, alkyl carboxylic acid esters having 3 to about 10 carbon atoms and mixtures thereof a partially crystalline polyester color concentrate having an inherent viscosity of at least 0.2 comprising:

(i) diacid residues comprised of at least 80 mole percent terephthalic acid residues, 2,6-naphthalenedicarboxylic acid residues, 1,3-cyclohexane-dicarboxylic acid residues, 1,4-cyclohexanedicarboxylic acid residues or a mixture thereof;

(ii) diol residues comprised of at least 50 mole percent of residues having the formula $-O-(CH_2)_p-O-$ wherein p is 2 to 12; and

(iii) at least 5.0 weight percent, based on the weight of the composition, residues of one or more thermally-stable, difunctional colorant compounds.

(2) precipitating from the solution of step (1) the semicrystalline colorant composition in a finely divided form comprised of particles having an average particle size of less than 50 microns.

30

15. A process according to Claim 14 wherein the partially crystalline polyester comprises:

- (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues, 2,6-naphthalenedicarboxylic acid residues, 1,3-cyclohexanedicarboxylic acid residues, 1,4-cyclohexanedicarboxylic acid residues or a mixture thereof;
- 5 (ii) diol residues comprised of at least 50 mole percent of residues having the formula $-O-(CH_2)_p-O-$ wherein p is 4 to 12; and
- 10 (iii) at least 5.0 weight percent, based on the weight of the composition, residues of one or more thermally-stable, difunctional colorant compounds copolymerized in the polyester.

15 16. A process according to Claim 14 wherein the partially crystalline polyester has an inherent viscosity of at least 0.2 and a melting temperature of at least 110°C and comprises:

- (i) diacid residues comprised of at least 80 mole percent terephthalic acid residues;
- 20 (ii) diol residues comprised of at least 80 mole percent of residues of 1,4-butanediol; and
- (iii) about 10 to 40 weight percent, based on the weight of the composition, residues of one or 25 more thermally-stable, difunctional, colorant compounds copolymerized in the polyester.

30 17. A process according to Claim 14 wherein step (1) comprises dissolving a melt of the partially crystalline polyester in an inert solvent selected from lower alkyl esters of aromatic mono- and dicarboxylic acids, or glycol esters of lower aliphatic carboxylic acids.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/07854

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C09B69/10; C08J3/09

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols		
Int.C1. 5	C09B ;	C08G ;	C08J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	WO,A,9 110 693 (EASTMAN KODAK) 25 July 1991 see page 38, line 1 - page 46, line 2 see examples 173,174,176 see examples 177,184,185 see comparative example 13 see claims 28-40 ---	1-17
P,X	EP,A,0 417 017 (EASTMAN KODAK) 13 March 1991 see page 2, line 49 - page 4, line 17 see page 9, line 17 - page 10, line 51 see examples 55,58,60 see examples 65-67 see claims 11-28 ---	1-17
A	WO,A,8 910 349 (EASTMAN KODAK) 2 November 1989 see page 9, line 27 - page 11, line 8; examples 6,7 ---	1 -/-

¹⁰ Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

¹¹ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹² document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹³ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art¹⁴ document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

2 13 FEBRUARY 1992

Date of Mailing of this International Search Report

05 MAR 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

KETTERER M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	WO,A,8 907 118 (EASTMAN KODAK) 10 August 1989 see claims 1-4; examples 1-4 ---	1-8
A	US,A,4 808 677 (M. A. WEAVER; C. A. COATES; W. P. PRUETT; S. D. HILBERT) 28 February 1989 see column 1, line 49 - column 2, line 36 see column 5, line 54 - column 8, line 3; examples 2,14,32,44-47 see examples 51,55,56 ---	1-8
A	EP,A,0 040 139 (EASTMAN KODAK) 18 November 1981 see page 1, line 23 - page 2, line 21 see page 9, line 25 - page 10, line 5; example 1 ---	1-8
A	DE,A,3 005 223 (EASTMAN KODAK) 4 September 1980 see page 14, line 9 - page 15, line 25 see examples 3-8 ---	1-8

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9107854
SA 53808

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9110693	25-07-91	EP-A-	0462262	27-12-91
EP-A-0417017	13-03-91	US-A- WO-A-	5032670 9103508	16-07-91 21-03-91
WO-A-8910349	02-11-89	US-A- EP-A- US-A- US-A-	4958043 0412101 5068348 5075491	18-09-90 13-02-91 26-11-91 24-12-91
WO-A-8907118	10-08-89	US-A- EP-A- JP-T-	4804719 0400038 3502339	14-02-89 05-12-90 30-05-91
US-A-4808677	28-02-89	None		
EP-A-0040139	18-11-81	JP-A- US-A-	57003851 4359570	09-01-82 16-11-82
DE-A-3005223	04-09-80	US-A- CA-A- FR-A,B GB-A,B JP-A- NL-A-	4267306 1130804 2450848 2046768 55112234 8000938	12-05-81 31-08-82 03-10-80 19-11-80 29-08-80 19-08-80